Electronic Supplementary Material (ESI) for Environmental Science: Nano.

Supplementary Information

Biomimetically Synthesized Luminescent Tb^{3+}-Doped Fluorapatite/Agar Nanocomposite for Detecting UO_2^{2+}, Cu^{2+}, and Cr^{3+} Ions

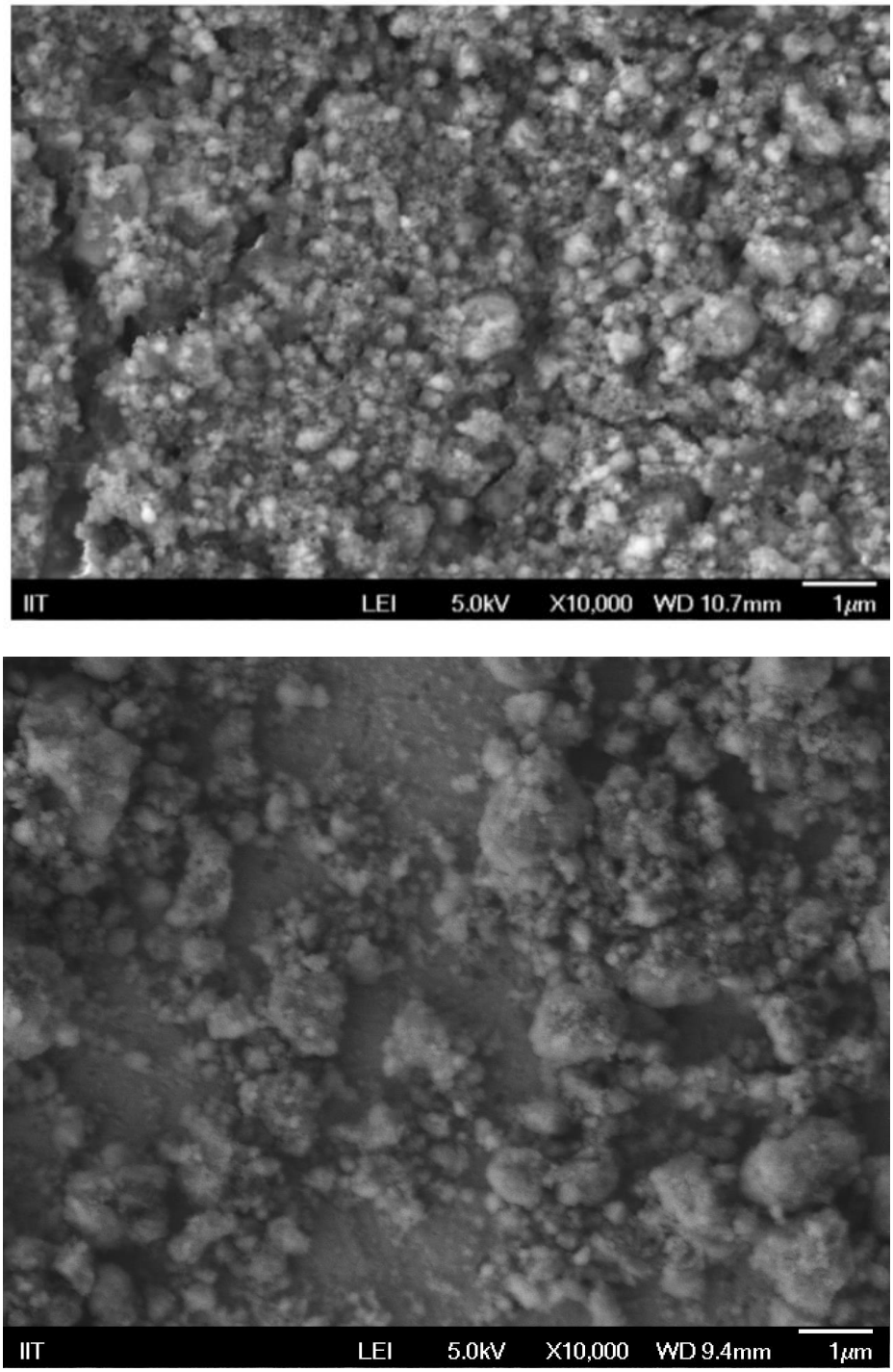


Figure S1. SEM images of the Tb-HAP/agar sample.

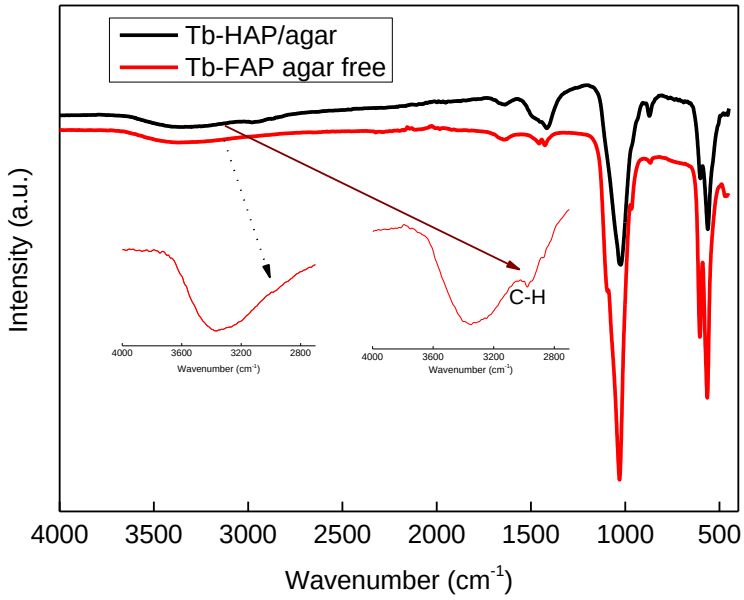


Figure S2. The FT-IR spectra of the Tb-HAP/agar and Tb-FAP agar free samples.

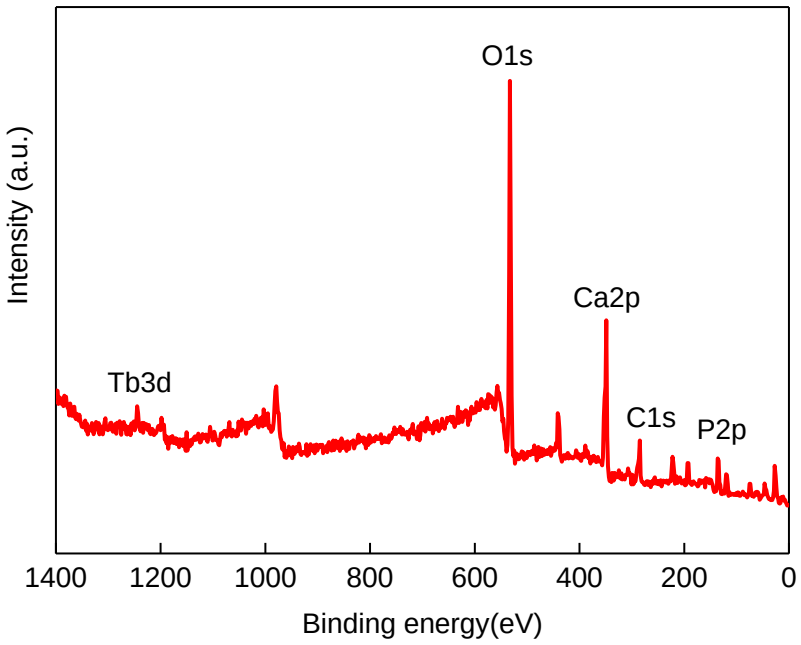


Figure S3. Survey scan of the XPS spectrum of the Tb-HAP/agar sample.

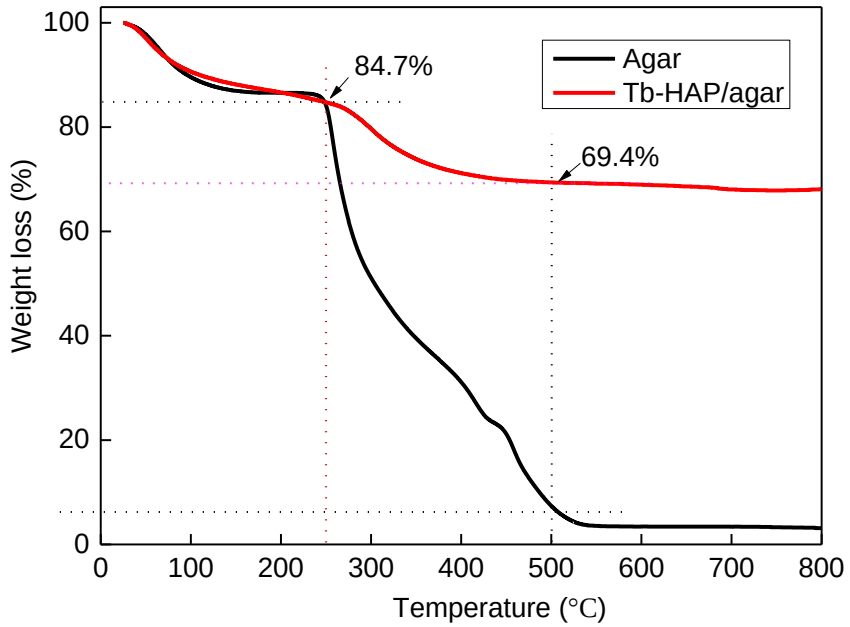


Figure S4. TGA plots of the Tb-HAP/agar and agar samples.

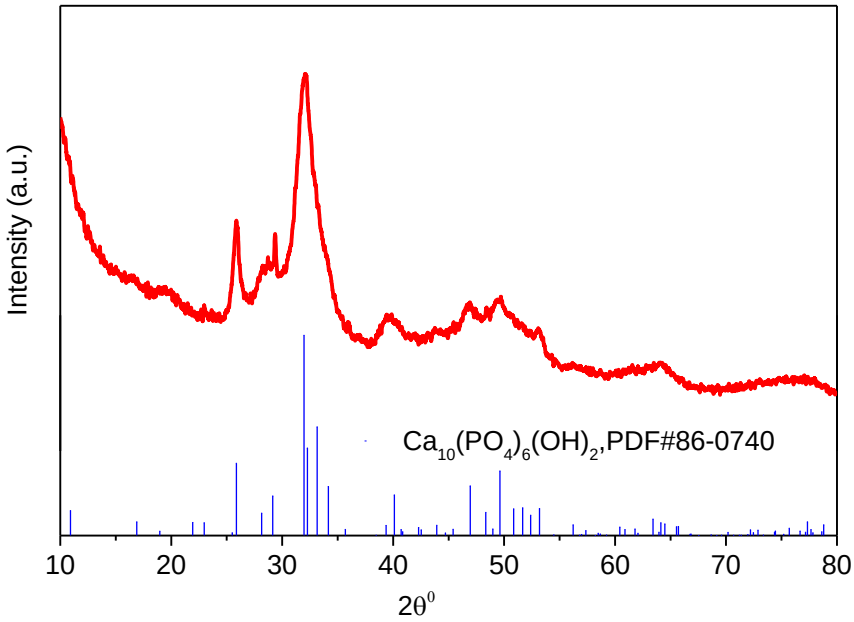


Figure S5. XRD pattern of the Tb-HAP/agar sample accompanying with the standard pattern (PDF#86-0740).

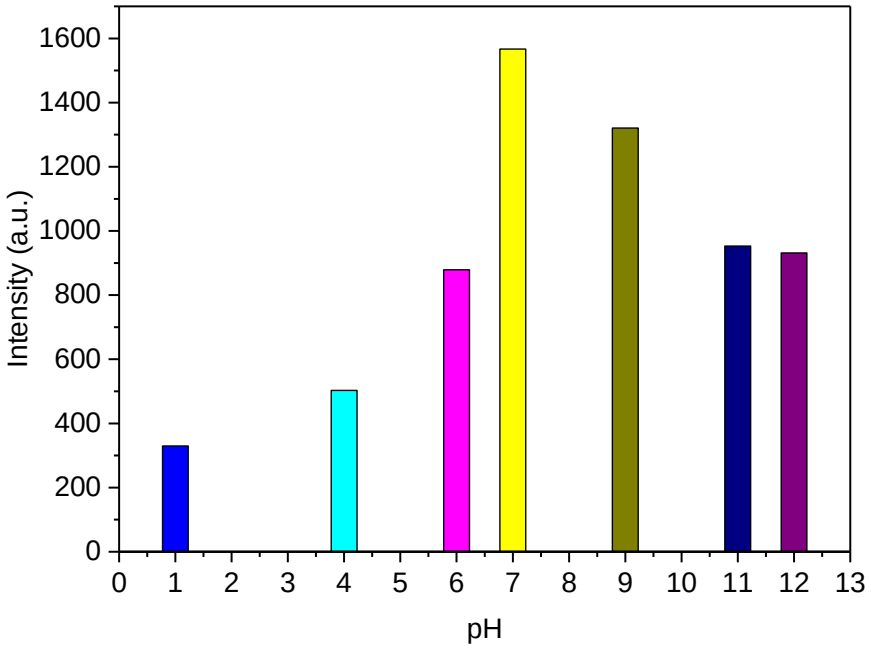


Figure S6. Effect of pH on the fluorescence intensity of Tb-FAP/agar samples.

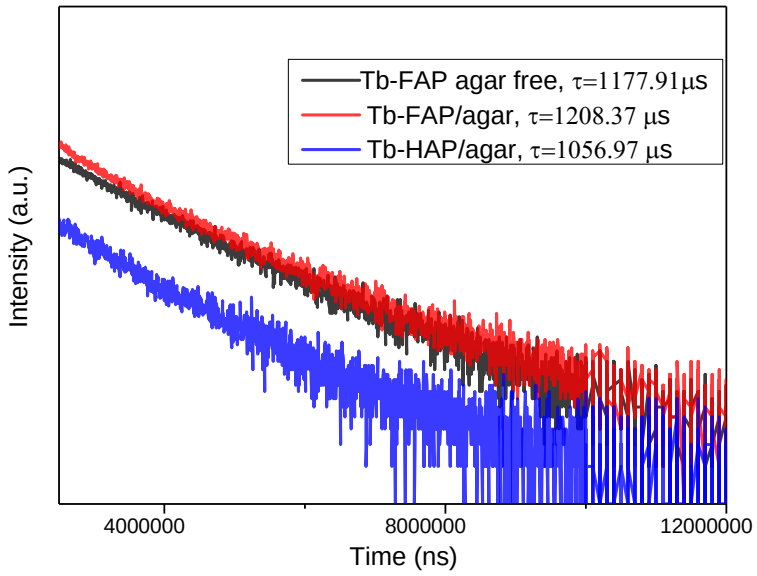


Figure S7. Luminescence lifetime curves of the Tb-FAP/agar, Tb-FAP agar free and Tb-HAP/agar samples (λ_{ex} = 377 nm and λ_{em} = 543 nm).

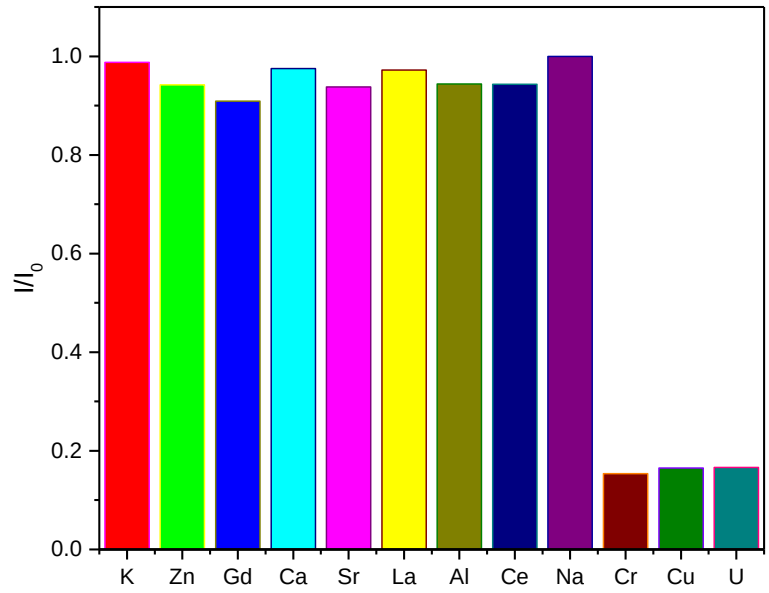


Figure S8. Luminescence intensity ratio of the Tb^{3+} $^5D_4 \rightarrow {}^7F_4$ transition (543 nm) of the Tb-FAP/agar sample (2.5 mL) after and before treated with different metal ions. (K^+, Zn^{2+}, Gd^{3+}, Ca^{2+}, Sr^{2+}, La^{3+}, Al^{3+}, Ce^{3+}, Na^+ ions, 100 uL, 0.01 M), and (UO_2^{2+}, Cu^{2+}, Cr^{3+} ions,10 uL, 0.01 M).

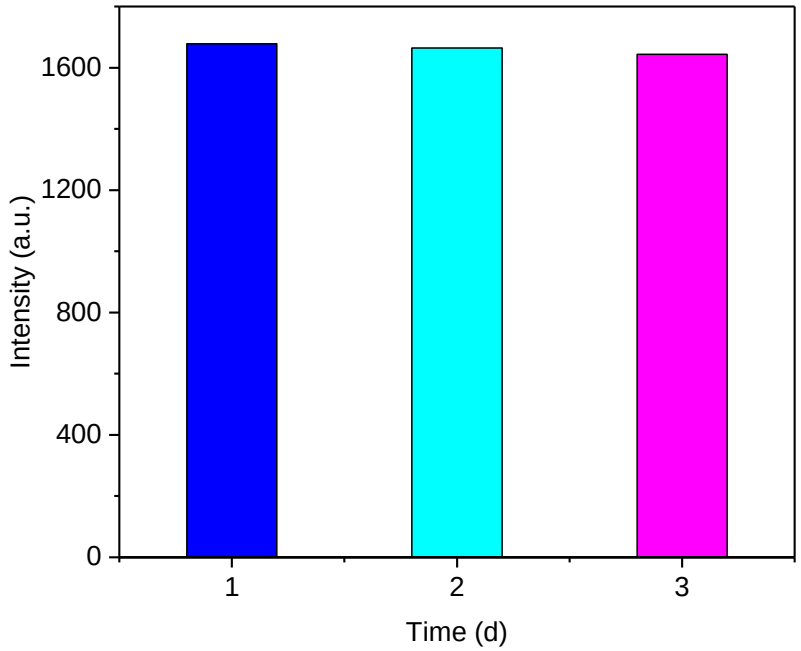


Figure S9. Luminescent intensities of the Tb-FAP/agar sample with the increase of storage time (without adding UO_2^{2+}, Cu^{2+}, and Cr^{3+} ions).

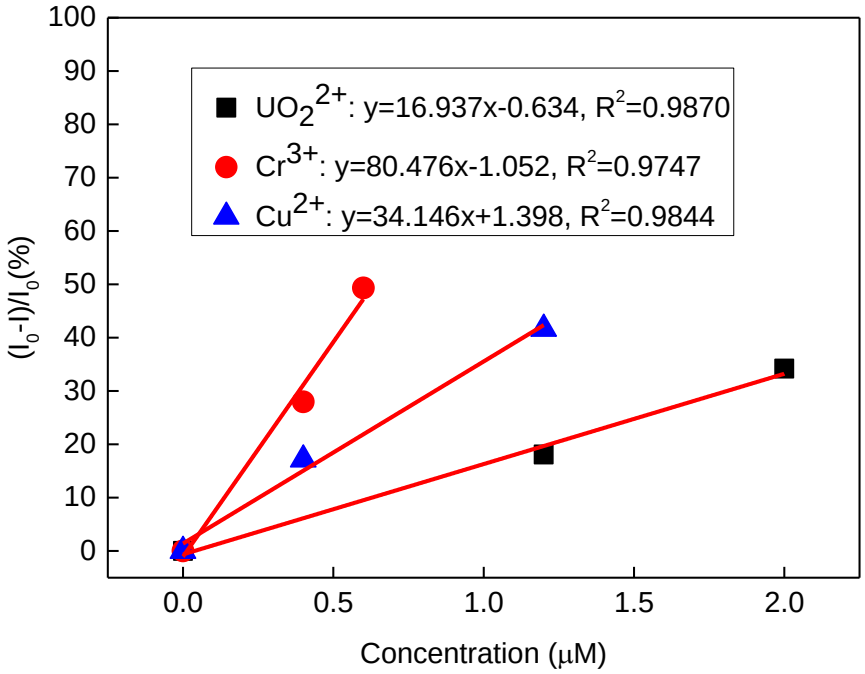


Figure S10. The linear fitting relationships between (I_0 - I)/I_0 and the concentration of UO_2^{2+}, Cr^{3+}, and Cu^{2+} ions.

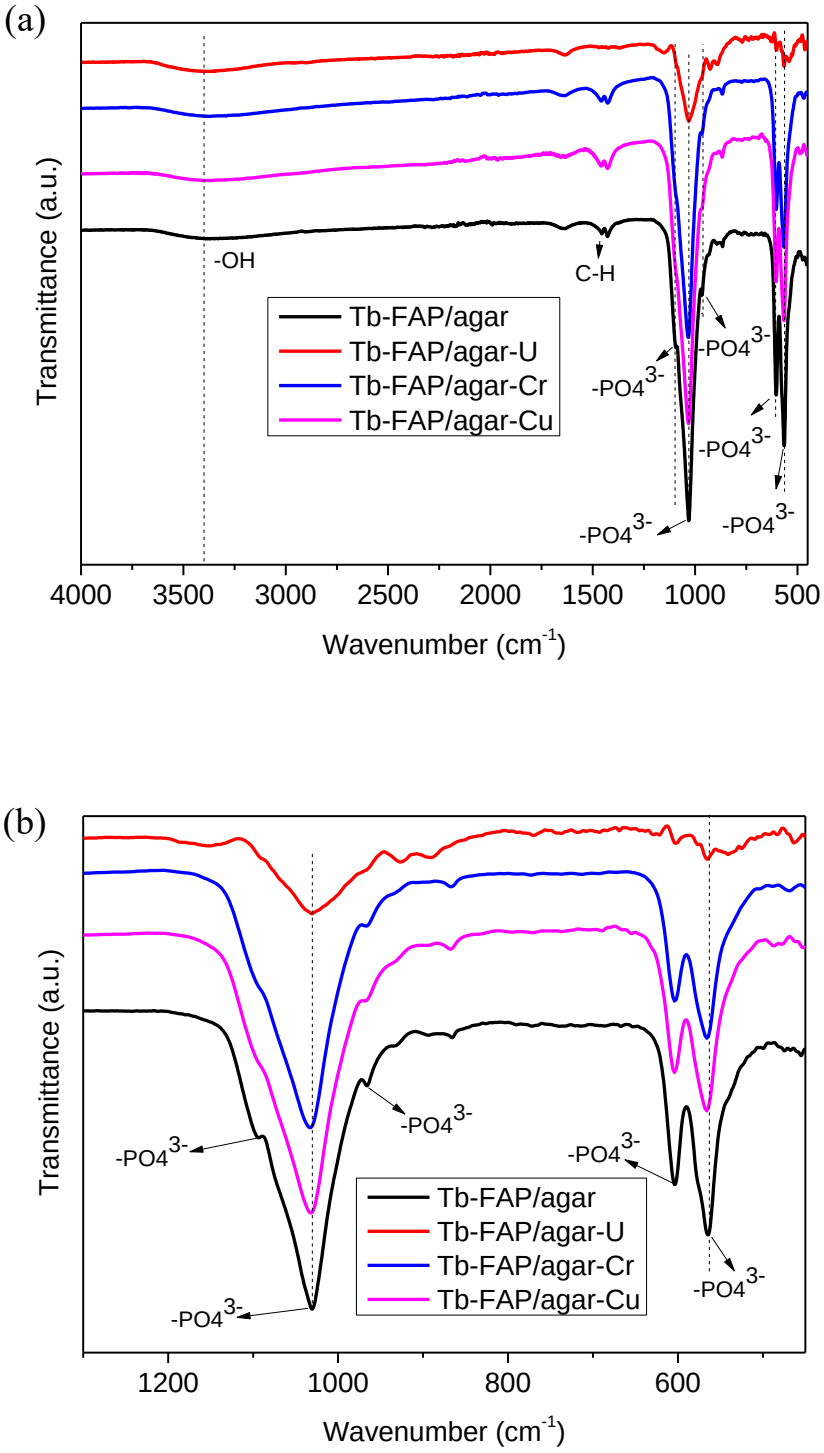
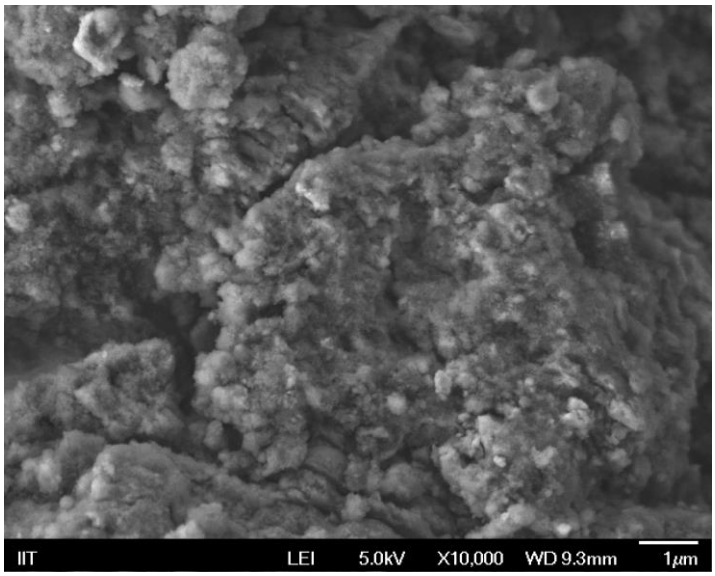
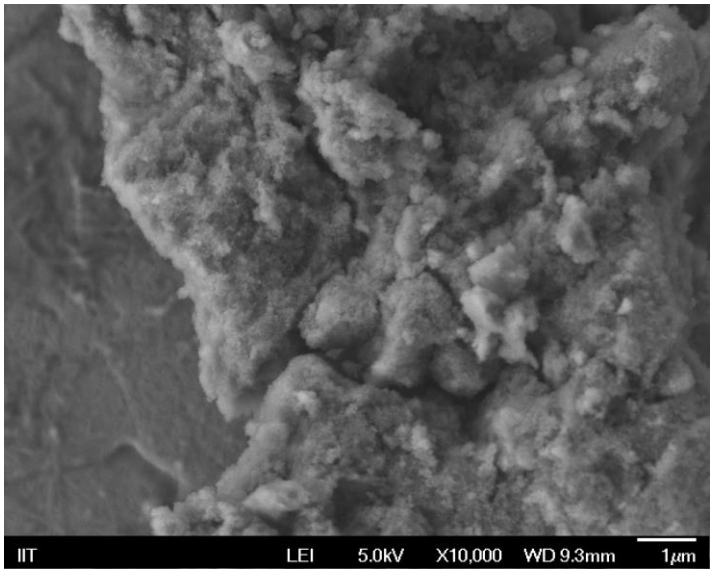


Figure S11. (a) FTIR spectra of the Tb-FAP/agar after treated with UO_2^{2+}, Cu^{2+} and Cr^{3+}. (b) The enlargement of the FTIR spectra in (a) with the wavenumber ranging from 450 cm^{-1} to 1300 cm^{-1} to more intuitively indicate the location of the PO_4^{3-} peaks.

(a)



(b)



(c)

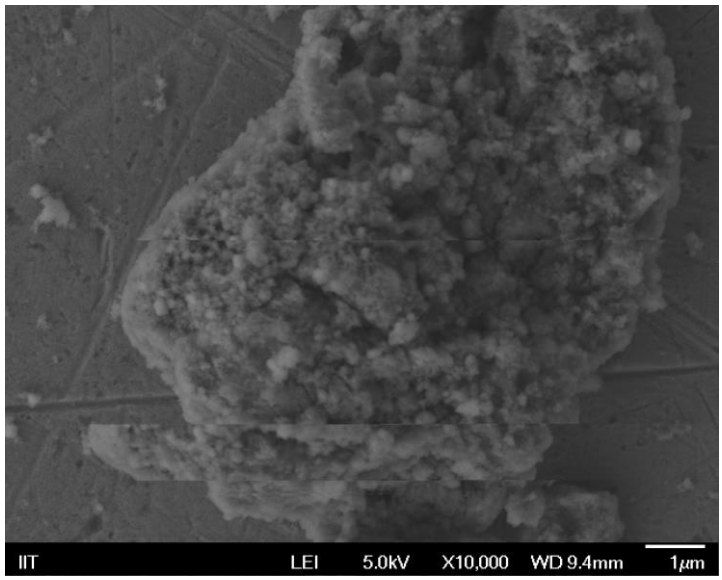


Figure S12. SEM images of the Tb-HAP/agar sample after treated with (a) UO_2^{2+}, (b) Cu^{2+}, and (c) Cr^{3+} solutions.

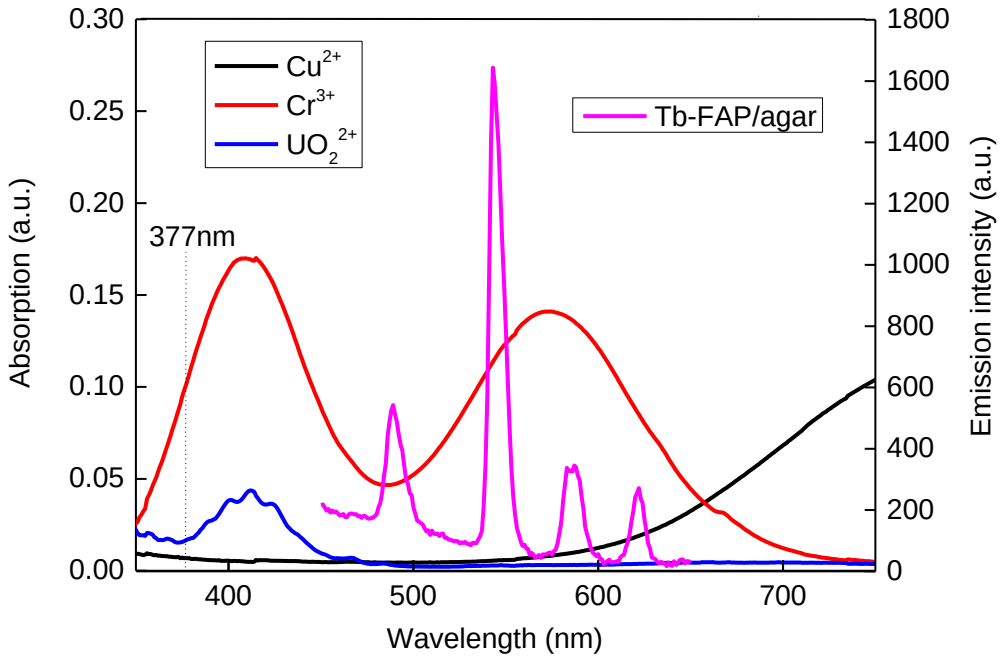


Figure S13. The luminescence spectrum of the Tb-FAP/agar sample and the UV-Vis spectra of $Cu(NO_3)_2 \cdot 3H_2O$, $Cr(NO_3)_3 \cdot 9H_2O$, and $(UO_2)(NO_3)_2$ aqueous solutions.

Table S1. Fitting parameters of the luminescence lifetime curves of the Tb-FAP/agar, Tb-FAP agar free and Tb-HAP/agar samples.

Parameters	τ_1 (μs)	τ_2 (μs)	A_1	A_2	τ_{ave} (μs)	R^2
Tb-FAP/agar	1231.05	2.78	1170.62	9739.76	1208.37	0.9948
Tb-FAP agar free	1193.08	2.95	854	4466.57	1177.91	0.9955
Tb-HAP/agar	1107.45	2.68	292.99	5798.67	1056.97	0.9941

Fitting parameters in Table S1 were obtained by using the following biexponential lifetime decay function:

$y = A_1 * \exp(-x/\tau_1) + A_2 * \exp(-x/\tau_2) + y_0$

τ_{ave} values were calculated according to the equation:

$\tau_{ave} = (A_1 * \tau_1^2 + A_2 * \tau_2^2)/(A_1 * \tau_1 + A_2 * \tau_2)$

Table S2. Fitting parameters of luminescence lifetime curves in the absence and presence of metallic ion aqueous solutions

Parameters	τ_1 (μs)	τ_2 (μs)	A_1	A_2	τ_{ave} (μs)	R^2
Tb-FAP/agar	1231.05	2.78	1170.62	9739.76	1208.37	0.9948
Tb-FAP/agar + 7.2 μM Cu^{2+}	718.00	3.23	566.74	8938.66	670.59	0.9854
Tb-FAP/agar + 5.7 μM Cr^{3+}	593.46	3.12	457.79	8808.25	539.26	0.9872
Tb-FAP/agar + 20 μM UO_2^{2+}	95.13	2.97	756.81	8815.26	70.55	0.9915

Table S3. Average luminescence lifetimes of the Tb-FAP/agar sample in the presence of different metal ions

Metal ions	No ions	Al^{3+}	K^+	Sr^{2+}	Ca^{2+}	Ce^{3+}	Gd^{3+}
T_{ave} (μs)	1208.37	1208.49	1211.96	1198.27	1197.53	1188.76	1161.52
Metal ions	La^{3+}	Na^+	Zn^{2+}	Cu^{2+}	Cr^{3+}	UO_2^{2+}	
T_{ave} (μs)	1166.84	1136.73	1177.84	670.59	539.26	70.55	

Determination of thee limit of detection (LOD) value:

The LOD values of the UO_2^{2+}, Cr^{3+}, and Cu^{2+} ions were determined based on the luminescence measurements shown in Figure S6. The linear domain of the low concentration range can be fitted as:

For UO_2^{2+} ions: $y = 16.937x - 0.634$, $R^2 = 0.9870$

For Cu^{2+} ions: $y = 34.146x + 1.398$, $R^2 = 0.9844$

For Cr^{3+} ions: $y = 80.476x - 1.052$, $R^2 = 0.9747$

where y is the quenching ratio of luminescence emission intensity [$100 \times (I_0\text{-}I)/I_0$)] at 543 nm, and x is the UO_2^{2+}, Cr^{3+}, and Cu^{2+} concentration. The standard deviation (σ) is defined as $100 \times (I_{SE}/I_0)$, where I_{SE} is the standard error of the emission measurement of the solution without the Tb-FAP/agar sample and any ions monitored at 543 nm. I_0 is the luminescence intensity of the Tb-FAP/agar sample in deionized water measured at 543 nm. If defining eleven times of the standard deviation as the detectable signal, the LOD values can be calculated as:

3σ/slope (UO_2^{2+}) = 7.95 nM (2.15 μg/L)

3σ/slope (Cu^{2+}) = 3.94 nM (0.25 μg/L)

3σ/slope (Cr^{3+}) = 1.67 nM (0.087 μg/L)